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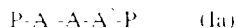
97 04 24 97 DE 101 7371 (98 10 29) C08G 63/21, 63/11, 63/54, 63/00, 63/66, 64/22, 64/26, 73/16, C09D 11/02, 167/07, 169/00, C09K 19/38

Propargyl-terminated nematic or cholesteric polymers - comprise polyester or polycarbonate with propargyl end-groups, or mixtures thereof, crosslinkable in the liquid crystal phase to give special pigments

C98-171334

Addnl. Data: SCHUHMACHER P. KRICHELDORF H R. GERKEN A

Propargyl-terminated nematic or cholesteric polyesters, polycarbonates or mixtures thereof (I) are new, except for diesters of formula (Ia).



A = 1,4-phenylene (Phe), 4,4'-biphenylene, 2,6-naphthylene or -Phe-CR=CR-Phe- (with R = H or CH₃) (all optionally substituted with halogen, nitro, alkyl, alkoxy, fluoroalkyl, fluoroalkoxy or phenyl);

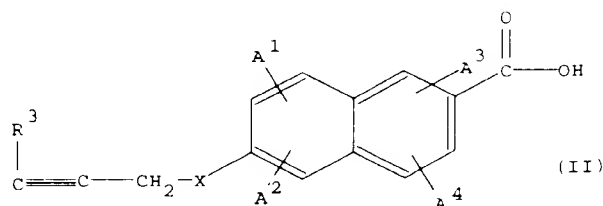
A¹, A² = -Phe-COO- or -Phe-OCO-; and

P = HC≡C-CH₂-O-

A¹-E1D, 5-E6B, 12-B1H, 12-W7D) E10-A25B1, 10-B2B, 10-C4B, 10-D3D) G02-A2E, 2-A4A)

Also claimed are

- (i) crosslinked polyesters or polycarbonates or nematic or cholesteric mixtures thereof obtained by heating (I);
(ii) pigments and coating materials containing (I) or crosslinked (I) and
(iii) compounds of formula (II) or their amides or acid halides.



A¹-A⁴ = H, alkyl, alkoxyalkyl, optionally alkyl-substituted cycloalkyl, halogen or nitro, preferably H;

X = S, O or NR²;

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R¹ = H, 1-4C alkyl or phenyl; and
R² = H, 1-4C alkyl, aryl or aryl-(1-4C alkyl).

USE

(I) are used as optical components, surface coating materials and colouring agents, especially as colour pigments in paint systems for coating surfaces or as components of printing ink (claimed). (II) are used as thermally or photochemically crosslinkable end-groups in polymers (claimed).

ADVANTAGE

(I) can be fixed by thermal crosslinking in the nematic or cholesteric (liquid crystal: LC) phase, to give LC pigments with special colour effects.

PREFERRED POLYMERS

(I) have at least one propargyl endgroup of formula R¹C≡C-CH₂- which is attached to the polyester or polycarbonate either directly (preferably to a hydroxyl end group) or via a linking group, preferably -O-, -S-, -NR²-, -O-Phe-X-, -OC-Phe-X-, -O-Nap-X- or -OC-Nap-X- (with the propargyl group attached to X), in which R¹ = H, 1-4C alkyl or phenyl; X = O, S or NR²; and Nap = 2,6-naphthylene.

Polyesters (I) contain (a) aromatic and/or araliphatic diacid and/or

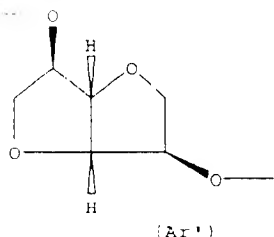
hydroxy-carboxylic acid unit(s) and (b) diol unit(s). Six suitable diacid units are listed, of which the preferred units are -OC-Nap-CO-, -OC-Phe-CO- and -OC-Phe-W-Phe-CO-, in which W = NR, S, O, (CH₂)_n, O-(CH₂)_q, (CH₂)_m or a single bond; R = H or alkyl; m = 1-15; p, q = 0-10; and in which each Phe or Nap group may be substituted with 1, 2 or 3 groups selected from 1-4C alkyl or alkoxy, halogen or phenyl.

Suitable hydroxy-acid units are -O-Phe-CO-, -O-Nap-CO- and -O-Phe-Phe-CO- (optionally substituted as above).

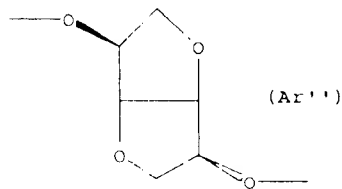
13 diol units are listed, including 9 preferred units of formula -O-Ar-O-, in which Ar = Phe or a Phe group substituted in position 2 with methyl, phenyl, tert-butyl, -S-CH₂-CHMeEt or -S-(CH₂)₃-CH₃, or Ar = a group of formula (Ar') or (Ar'').

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(Ar')



(Ar'')

(optionally substituted as above), and A = diol units as above.

Preferred diesters have the formula HC≡C-CH₂-O-B-COO-A, OCO-B-OCH₂-C≡CH, with B = unsubstituted -Nap- or -Phe-Phe-, and A = Ar', Ar'', -Phe- or -Phe- substituted in position 2 with Me, Ph, -S-(CH₂)₃-CH₃ or -S-CH₂-CHMeEt.

Polycarbonates (I) contain diol unit(s) as above, especially -O-Phe-Phe-O-, -O-Phe-O- (optionally with Me at position 2), -O-Ar'-O- or -O-Ar''-O-, preferably at least one mesogenic unit of formula -O-Phe-Phe-O- or -O-Phe-COO-Phe-O-, at least one chiral unit of formula -O-Ar'-O- or -O-Ar''-O- and optionally a non-chiral unit of formula -O-

Ar' or Ar'' as above, the propargyl group in these polyesters is attached via -O-, -O-Phe-X- or -OC-Nap-X- (with X = O or S). Diesters of this type have the formula P-Y-B-COO-A-OCO-B-Y-P, in which P = propargyl as above, Y = O, S or NR² (R² = 1-4C alkyl).

PREFERRED PRODUCTS

Crosslinked products are obtained by heating (I) at 120-340

(preferably 200-315°C, preferably in presence of a catalyst, especially $\text{CpCo}(\text{CO})_2$, CuCl , CuCl_2 , Cp_2Ni , $(\text{Ph}_3\text{P})_3\text{NiCl}$ or $\text{RhCl}(\text{PPh}_3)_3$ (with Cp = cyclopentadienyl), in amounts of 0.01-3 (preferably 0.1-1) wt.% based on the reaction mixture.

PREPARATION

(I) are obtained by standard polycondensation methods, e.g. by reacting free diols with diacid chlorides and propargyl derivatives with a free hydroxyl function or chlorides of propargyl derivatives in a suitable solvent.

STARTING MATERIALS

Propargyl derivatives (II) are obtained by standard methods, e.g. by reacting propargyl chloride with the K salt of a hydroxy-aromatic acid.

EXAMPLE

A mixture of 20 mmols isosorbide, 41 mmols 4'-propargyloxy-4-phenyl-benzoyl chloride (obtained by reacting propargyl chloride with potassium hydroxyphenyl-benzoate in aqueous solution and reacting the acid obtained with SOCl_2) and 100 ml CHCl_3 was treated with a solution of 41 mmols pyridine in 10 ml CHCl_3 , and stirred for 24

hours under N_2 at room temperature. The mixture was diluted with 100 ml CHCl_3 , washed with 1N-HCl and water, and worked up by evaporation under vacuum followed by precipitation with ligroin, to give a diester (3a) of formula $\text{HC}\equiv\text{C}-\text{CH}_2\text{O}-\text{Phe}-\text{Phe}-\text{COO}-\text{A}-\text{OCO}-\text{Phe}-\text{Phe}-\text{OCH}_2\text{C}\equiv\text{CH}$ (with A = isosorbide residue), in a yield of 46%. This product showed a m.pt. (T_m) of 170°C and a crosslinking temperature (T_x) of 301°C. The melt was isotropic.

Another diester (3c) with A = 2-methyl-1,4-phenylene was obtained in 78% yield by a similar method from 2-methylhydroquinone; this product showed a T_m of 220°C, a clearing point (T_i) of above 300°C and a T_x of 303°C. The melt was enantiotropic nematic, with a homeotropic schlieren texture.

A mixture of 10 mol% (3a) and 90 mol% (3c) showed a T_i of more than 300°C, and was crosslinkable in the liquid crystal phase. It formed an enantiotropic cholesteric melt with a Grandjean structure, showing all colours of the rainbow and becoming blue-green after crosslinking. (HW)
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